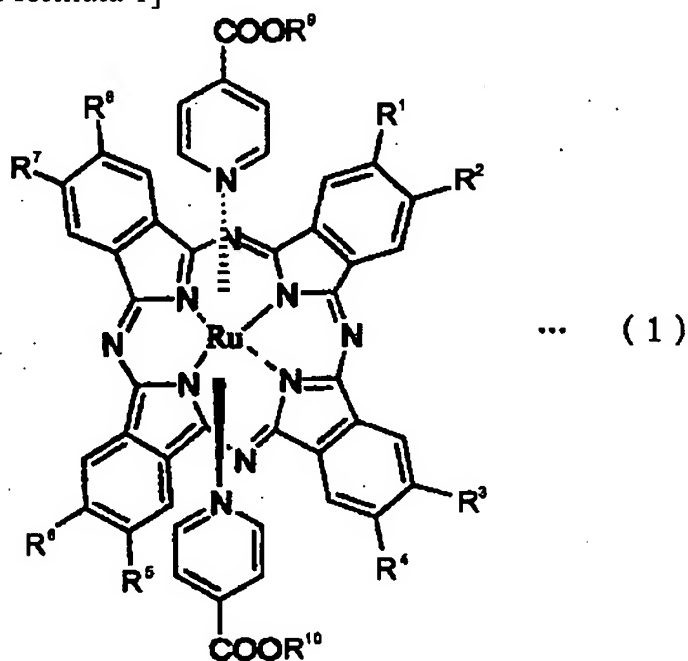


FULL CONTENTS

[Claim(s)]

[Claim 1] A general formula (1);

[Chemical formula 1]



(R¹ - R⁸ are one sort chosen from hydrogen, halogen, t-butyl group, a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, respectively, and)

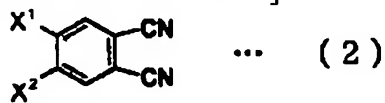
[**] And a RUTENIUMU phthalocyanine derivative by which one sort; R⁹ and R¹⁰ as which at least one of R¹ - R⁸ is chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine are expressed with hydrogen or an ethyl group, respectively.

[Claim 2] the inside of said formula (1), and inside of R¹ and R² -- on the other hand -- inside of R³ and R⁴ -- on the other hand -- inside of R⁵ and R⁶ -- on the other hand -- and among R⁷ and R⁸, [one side] The RUTENIUMU phthalocyanine derivative according to claim 1 in which it is one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, respectively, and each another side is hydrogen or halogen, respectively.

[Claim 3] the inside of said formula (1), and inside of R¹ and R² -- on the other hand -- inside of R³ and R⁴ -- on the other hand -- inside of R⁵ and R⁶ -- on the other hand -- and among R⁷ and R⁸, [one side] The RUTENIUMU phthalocyanine derivative according to claim 1 in which it is one sort altogether chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, and each another side is hydrogen or halogen, respectively.

[Claim 4] A general formula (2);

[Chemical formula 2]



X¹ and X² -- respectively -- hydrogen, halogen, and t-butyl group. They are one or more sorts of phthalocyanine

nitrile derivatives denoted by one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, A phtalo nitrile derivative whose at least one sort in this phtalo nitrile derivative is one sort as which either [at least] X^1 in said formula (2) or X^2 is chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, and a general formula (3);

[Chemical formula 3]



A manufacturing method of a RUTENIUMU phthalocyanine derivative, wherein (X^3 makes the isonicotinic acid derivative denoted by hydrogen or ethyl group) react under existence of RUTENIUMU salt.

[Claim 5] A manufacturing method of the RUTENIUMU phthalocyanine derivative according to claim 4 whose X^1 is one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine among said formula (2) and whose X^2 is hydrogen or halogen.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a new RUTENIUMU phthalocyanine derivative and a manufacturing method for the same.

[0002]

[Description of the Prior Art] Phthalocyanines are high and the application range has heat stability and very large chemical stability. Especially the ruthenium complex of phthalocyanines is excellent in the light energy utilization efficiency over sunlight. The utilization efficiency of light energy can be judged to some extent from the height of ***** in the wide wavelength range, i.e., the height of the absorption efficiency of light energy.

[0003]

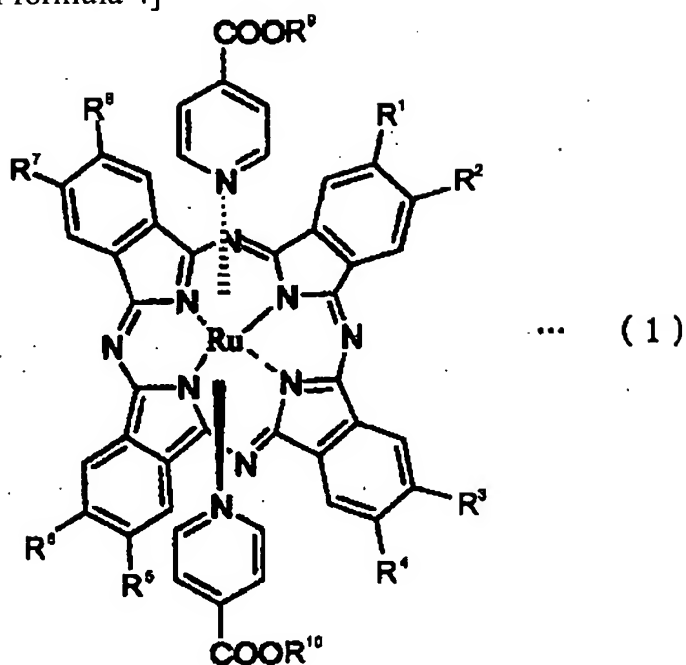
[Problem to be solved by the invention] Therefore, let it to provide a new RUTENIUMU phthalocyanine derivative which realizes broad absorption of sunlight more, and a manufacturing method for the same be the issue which should be solved in this invention.

[0004]

[Means for solving problem] When this invention persons introduced various substituents into the RUTENIUMU phthalocyanine derivative in order to solve above-mentioned SUBJECT, the optical absorption efficiency was examined, and the high substituent of electron release nature was introduced, the optical absorption spectrum shifted to the long wavelength side, and it became clear that it broadcloth-ized. It found out that-izing of the optical absorption spectrum could be especially carried out [broadcloth] to a RUTENIUMU phthalocyanine derivative remarkably by introducing a morpholino group, 4-ethoxycarbonyl piperidino machine, or 4-KARUBOKISHI piperidino machine, and thought out to this invention. That is, the RUTENIUMU phthalocyanine derivative of this invention is a general formula (1).;

[0005]

[Chemical formula 4]



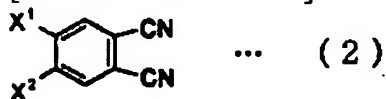
[0006](R¹ - R⁸ are one sort chosen from hydrogen, halogen, t-butyl group, a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, respectively, and) [**] And one sort; R⁹ and R¹⁰ as which at least one of R¹ - R⁸ is chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine are denoted by hydrogen or an ethyl group, respectively.

[0007]On the other hand, among said formula (1) and among R¹ and R², among R³ and R⁴ And R⁵. On the other hand, among R⁵ and R⁶, among R⁷ and R⁸ in a row, [one side] It is preferred that it is one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, respectively, and, [these] It is more preferred to be unified only by one sort altogether chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine. In this case, as for each another side, it is preferred that they are hydrogen or halogen, respectively.

[0008]The manufacturing method of the RUTENIUMU phthalocyanine derivative of this invention which solves above-mentioned SUBJECT is a general formula (2).;

[0009]

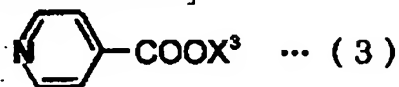
[Chemical formula 5]



[0010]X¹ and X² -- respectively -- hydrogen, halogen, and t-butyl group. They are one or more sorts of phthalonitrile derivatives denoted by one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, The phthalonitrile derivative whose at least one sort in this phthalonitrile derivative is one sort as which either [at least] X¹ in said formula (2) or X² is chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, and general formula (3);

[0011]

[Chemical formula 6]



[0012](X³ makes the isonicotinic acid derivative denoted by hydrogen or ethyl group) react under existence of RUTENIUM salt.

[0013]And X¹ is one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine among said formula (2), and, as for X², it is preferred that they are hydrogen or halogen.

[0014]

[Mode for carrying out the invention]The substituent denoted by R¹ - R⁸ in a formula (1) is one sort independently chosen from hydrogen, halogen, t-butyl group, a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, respectively. Here, although halogen in particular is not limited, the viewpoints of the availability of a materials compound, the ease of carrying out of a reaction, etc. to chlorine is preferred.

[0015]In the substituent which shows hydrogen quoted here, t-butyl group, a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine later according to this order, electron release nature goes up. Since it has become clear that the optical absorption spectrum to sunlight becomes broadcloth, [the RUTENIUM phthalocyanine derivative which introduced the high substituent of electron release nature as a result of an inventor's etc. examination] The substituent denoted by R¹ - R⁸ t-butyl group, a morpholino group, It is preferred to be chosen from the group which consists of a 4-ethoxycarbonyl piperidino machine and a 4-KARUBOKISHI piperidino machine, It is more preferred to be chosen from the group which consists of a morpholino group, a 4-ethoxycarbonyl piperidino machine, and a 4-KARUBOKISHI piperidino machine, and it is still more preferred to be chosen from the group which consists of a 4-ethoxycarbonyl piperidino machine and a 4-KARUBOKISHI piperidino machine.

[0016]And at least one of R¹ - R⁸ is morpholino group, 4-KARUBOKISHI piperidino, or 4-ethoxycarbonyl piperidino machine machine. A highly efficient RUTENIUM phthalocyanine derivative is obtained by one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine being introduced as or more one substituent.

[0017]Since t-butyl group, a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine are bulky, they are difficult to introduce into the position where a phthalocyanine frame adjoins each other. Therefore, in introducing as a substituent one sort chosen from t-butyl group, a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine. It is preferred to introduce hydrogen or halogen into the adjoining position (R¹, R² and R³, R⁴ and R⁵, R⁶, R⁷ and R⁸), respectively, and also as for these all, it is more preferred to be unified with either one of hydrogen or halogen. When halogen is introduced here, there are being easy to compound (for example, the availability of materials, ease of a reaction, etc.) and a becoming advantage. And when hydrogen is introduced, it is desirable at the point which can reduce a molecular weight and whose optical absorption efficiency per unit weight improves.

[0018]And R⁹ and R¹⁰ are hydrogen or an ethyl group, respectively. It is preferred that it is hydrogen as R⁹ and R¹⁰. Especially the compound that made R⁹ and R¹⁰ the ethyl group has R⁹ and useful R¹⁰ as a

precursor of the compound which is hydrogen.

[0019]As a desirable RUTENIUMU phthalocyanine derivative, concretely The inside of a formula (1), R¹ the inside of 1 and R² -- on the other hand -- the inside of R³ and R⁴ -- on the other hand -- the inside of R⁵ and R⁶ -- on the other hand -- and among R⁷ and R⁸, [one side] It is a compound which is one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, respectively. It is the compound unified only by one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine more preferably [all]. And they are a compound whose substituent of the remainder of R¹ - R⁸ is hydrogen or halogen, and the compound in which all the more desirable substituents remaining [of R¹ - R⁸] were unified with either hydrogen or halogen.

[0020](Manufacturing method of a RUTENIUMU phthalocyanine derivative), [a manufacturing method of a RUTENIUMU phthalocyanine derivative of this invention] It is the method of manufacturing a RUTENIUMU phthalocyanine derivative denoted by a formula (1), and is a method to which a phtalo nitrile derivative denoted by a general formula (2) and an isonicotinic acid derivative denoted by a general formula (3) are made to react under existence of RUTENIUMU salt.

[0021]A substituent expressed with X¹ and X² to a formula (2) is one sort chosen from hydrogen, halogen, t-butyl group, a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine, respectively. Here, viewpoints of the availability of a compound, the ease of carrying out of a reaction, etc. to chlorine of halogen is preferred.

[0022]And chemical structure of a RUTENIUMU phthalocyanine derivative to manufacture can determine selection of X¹ and X². Namely. [R¹-R⁸ in a formula (1)] Not all substituents that a substituent introduced into X¹ and X² is introduced, and are introduced into X¹ and X² need to be the same, and a phtalo nitrile derivative which expressed with a formula (2) may be a mixture of two or more kinds of compounds. And. [a RUTENIUMU phthalocyanine derivative manufactured] [have / one sort per ** / at least / chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine] A compound which has one sort chosen as either X¹ and X² from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine also in a phtalo nitrile derivative which is materials is included. [X¹] [as one sort chosen from a morpholino group, 4-ethoxycarbonyl piperidino machine, and 4-KARUBOKISHI piperidino machine] [using for materials a phtalo nitrile derivative of a single kind which used X² as hydrogen or halogen] Inside of a formula (1) explained as a desirable RUTENIUMU phthalocyanine derivative, On the other hand, among R¹ and R², among R³ and R⁴ on the other hand, On the other hand, one side among R⁷ and R⁸ in a row among R⁵ and R⁶, respectively A morpholino group, It is one sort chosen from 4-ethoxycarbonyl piperidino machine and 4-KARUBOKISHI piperidino machine, and a compound whose substituent of the remainder of R¹ - R⁸ is hydrogen or halogen can be manufactured. If a compound which expressed with a formula (2) is used as one kind of compound, a RUTENIUMU phthalocyanine derivative of single structure can be manufactured mostly.

[0023][each group of R¹ which is a substituent of the adjoining position in a formula (1), R² and R³, R⁴ and R⁵, R⁶, and R⁷ and R⁸] Since it is supplied from the same molecule of a phtalo nitrile derivative denoted by a formula (2), the combination of the substituent of an adjoining position is controllable by the kind of substituent introduced into each of X¹ and X². [form / four groups of the substituent of the above-mentioned adjoining position are together put to it, and / the RUTENIUMU phthalocyanine

derivative of a formula (1)] Since the reaction of this manufacturing method may be unable to prescribe the position of the combination uniquely, A RUTENIUMU phthalocyanine derivative with the target chemical structure can be obtained by separating the manufactured RUTENIUMU phthalocyanine derivative by proper methods (solvent extraction, chromatography, etc.).

[0024]The phthalo nitrile derivative denoted by a formula (2) can be manufactured in accordance with a usual state method. For example, 4-nitroglycerine phthalo nitril, and 4 and 5-dichloro phthalo nitril, The compound which added hydrogen to the substituent to introduce into X^1 or X^2 (for example, to introduce a morpholino group into X^1 .) In acetonitrile morpholine at about 60-100 °C under existence of triethyl amine ("TEA" is called hereafter) (When 4 and 5-dichloro phthalo nitril is used as materials), Or in N and N'-JIMECHIRU formamide (DMF), under existence of sodium carbonate, it is made to react (when 4-nitroglycerine phthalo nitril is used as materials), and can manufacture at about 30-100 °C.

[0025] X^3 in a formula (3) is hydrogen, an ethyl group, i.e., isonicotinic acid, or isonicotinic acid ethyl, and is chosen according to the chemical constitution formula of the RUTENIUMU phthalocyanine derivative which also makes this selection the purpose. Specifically, it is chosen by R^9 in a formula (1), and R^{10} . After it introduces the ethyl group into X^3 at the time of a reaction and R^9 in a formula (1) and R^{10} obtain the RUTENIUMU phthalocyanine derivative which is an ethyl group, it can hydrolyze and R^9 and R^{10} can also obtain the RUTENIUMU phthalocyanine derivative which is hydrogen.

[0026]RUTENIUMU salt in particular is not limited. For example, $RuCl_3$, RuF_3 , etc. can be illustrated.

And as for RUTENIUMU, it is preferred that it is trivalent.

[0027]The RUTENIUMU phthalocyanine derivative made into the purpose by heating these phthalo nitrile derivatives, an isonicotinic acid derivative, and RUTENIUMU salt in a proper solvent is obtained. As a solvent, the solvent which are high-boiling points, such as 2-ethoxy ethanol, methoxy ethanol, and chloro NAFUTAREN, pen TANORU, 1, 2-dichlorobenzene, DMF, and DMSO, can be used. When using isonicotinic acid ethyl as an isonicotinic acid derivative denoted by a formula (3), it is also possible to use it as a solvent using an excessive quantity of isonicotinic acid ethyl.

[0028]In order to advance this reaction smoothly, it is preferred to carry out under heating. For example, about 130-300 °C is about 230-250 °C preferably. It is preferred to use catalysts, such as diazabicyclo UNDENSEN ("DBU" is called hereafter), quinoline, and $(NH_4)_2MoO_4$.

[0029]The target compound is obtained by refining the manufactured RUTENIUMU phthalocyanine derivative by a usual state method. For example, they are the selection extraction by a solvent, chromatography, etc.

[0030]

[Working example]An example is given and explained below about a RUTENIUMU phthalocyanine derivative of this invention, and a manufacturing method for the same. It cannot be overemphasized that a RUTENIUMU phthalocyanine derivative of this invention and a manufacturing method for the same are not the things which have the chemical constitution formula limited by the following illustration.

[0031](Reference example)

- It kept at 100 °C, agitating the mixture of 1.97 g of synthetic 4-nitroglycerine phthalo nitril of 4-morpholino phthalo nitril, 10mmol, 3.9 g of morpholine and 45mmol, and 3.18 g of sodium carbonate and 30mmol in DMF50mL. Vacuum concentration of the obtained output was carried out, and **** was refined in silica gel chromatography using ***** of ethyl acetate:hexane (= volume ratio 3:7). ****

was 65%.

[0032]- 4 -(4-KARUBOKISHI piperidino)- 1.97 g of synthetic 4-nitroglycerine phtalo nitril of phtalo nitril, and 10mmol, It kept at 60-100 **, agitating the mixture of 7 g of 4-KARUBOKISHI piperidine, 45mmol, and 6.3 g of sodium carbonate and 60mmol in DMF60mL. Vacuum concentration of the obtained output was carried out, and **** was refined in silica gel chromatography using ***** of ethyl acetate:hexane (= volume ratio 55:45). **** was 55%.

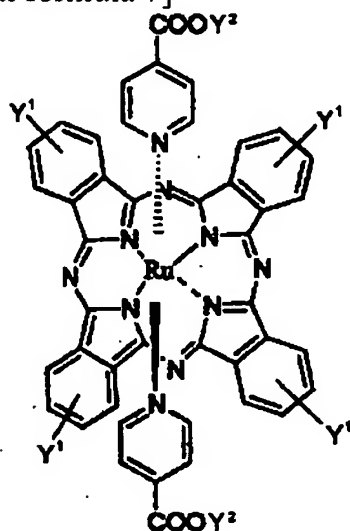
[0033]- 4 -(4-ethoxycarbonyl piperidino)- 1.97 g of synthetic 4-nitroglycerine phtalo nitril of phtalo nitril, and 10mmol, It kept at 80 **, agitating the mixture of 7 g of 4-ethoxycarbonyl piperidine, 45mmol, and 3.2 g of sodium carbonate and 30mmol in DMF60mL. Vacuum concentration of the obtained output was carried out, and **** was refined in silica gel chromatography using ***** of ethyl acetate:hexane (= volume ratio 55:45). **** was 50%.

[0034]- The mixture of the composition 4 of 4-morpholino 5-chloro phtalo nitril, 1.97 g of 5-dichloro phtalo nitril, 10mmol, 1.3 g of morpholine and 15mmol, and TEA1.5g and 15mmol was refluxed in acetonitrile 20mL for 6 to 8 hours. Vacuum concentration of the obtained output was carried out, and **** was refined in silica gel chromatography using ***** of ethyl acetate:hexane (= volume ratio 25:75). **** was 80%.

[0035](Synthetic example) The sample 1 - the sample 10 with the chemical structure expressed in a lower type (4) and Table 1 were compounded.

[0036]



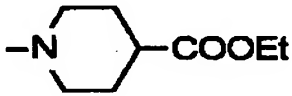
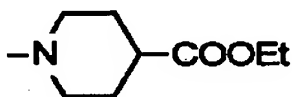
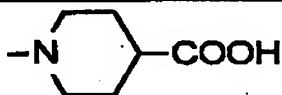
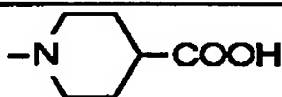
[Chemical formula 7]



... (4)

[0037]

[Table 1]

試料番号	Y ¹	Y ²
1	-H	-H
2	-H	-CH ₂ CH ₃
3	-C(CH ₃) ₃	-H
4	-C(CH ₃) ₃	-CH ₂ CH ₃
5		-H
6		-CH ₂ CH ₃
7		-H
8		-CH ₂ CH ₃
9		-H
10		-CH ₂ CH ₃

[0038]- With 200 mg and 1.0mmol, in phthalo nitril, isonicotinic acid was flowed back at 370 mg with 1 g and 8mmol, and 3mmol was flowed back [of the sample 1 / synthetic RuCl₃ and 3H₂O] for 4 hours in the mixture of the 2-ethoxy ethanol of DBU of 1.5mL, and 30mL. Then, evaporation removal of an excessive quantity of ethoxy ethanol was carried out, and the **** was ground using sulfuric acid 20%. The back according to ** dried the precipitation which deposited with the membrane filter. Various solvents extracted using Soxhlet extractor and the refined compound was obtained as an ether extract. **** was 45%.

[0039]- 2.4 g, 19mmol, and isonicotinic acid ethyl were flowed back [of the sample 2 / synthetic RuCl₃ and 3H₂O] in 5mL in phthalo nitril with 1.0 g and 5.0mmol for 4 hours. Then, evaporation removal of an excessive quantity of isonicotinic acid ethyl was carried out, and the **** was ground using sulfuric acid 20%. The back according to ** dried the precipitation which deposited with the membrane filter. Ethyl acetate: It refined using the alumina column using ***** of hexane (it is 1:4 at = volume ratio). **** was 60%.

[0040]- It replaced with the synthetic phthalo nitril of the sample 3, and carried out in the synthesizing method of the above-mentioned sample 1, and the similar way except having used 4-tert-butyl phthalo nitril. **** was 55%.

[0041]- It replaced with the synthetic phthalo nitril of the sample 4, and carried out in the synthesizing method of the above-mentioned sample 2, and the similar way except having used 4-tert-butyl phthalo

nitril. **** was 75%.

[0042]- It replaced with the synthetic phtalo nitril of the sample 5, and carried out in the synthesizing method of the above-mentioned sample 1, and the similar way except having used 4-morpholino phtalo nitril. **** was 37%.

[0043]- It replaced with the synthetic phtalo nitril of the sample 6, and carried out in the synthesizing method of the above-mentioned sample 2, and the similar way except having used 4-morpholino phtalo nitril. **** was 45%.

[0044]- Replace with the synthetic phtalo nitril of the sample 7, and it is 4. -(4-ethoxycarbonyl piperidino)- It carried out in the synthesizing method of the above-mentioned sample 1, and the similar way except having used phtalo nitril. **** was 38%.

[0045]- Replace with the synthetic phtalo nitril of the sample 8, and it is 4. -(4-ethoxycarbonyl piperidino)- It carried out in the synthesizing method of the above-mentioned sample 2, and the similar way except having used phtalo nitril. **** was 45%.

[0046]- Replace with the synthetic phtalo nitril of the sample 9, and it is 4. -(4-KARUBOKISHI piperidino)- It carried out in the synthesizing method of the above-mentioned sample 1, and the similar way except having used phtalo nitril. **** was 30%.

[0047]- Replace with the synthetic phtalo nitril of the sample 10, and it is 4. -(4-KARUBOKISHI piperidino)- It carried out in the synthesizing method of the above-mentioned sample 2, and the similar way except having used phtalo nitril. **** was 35%.

[0048]- In addition to this, it replaced with the synthetic phtalo nitril of a sample, and carried out in the synthesizing method of the above-mentioned sample 1, and the similar way except having used 4-morpholino 5-chloro phtalo nitril. **** was 55%. This result shows that this manufacturing method is applicable, even if the substituent is introduced into the both sides of X^1 in said formula (2), and X^2 .

[0049](Measurement of optical absorption efficiency) In order to measure optical absorption efficiency, ***** in a light range (450-900 nm) was measured about the samples 1, 3, 5, 7, and 9. Into DMF, it was made to dissolve by the concentration of 7.5×10^{-5} mol/L, and measurement went.

[0050]The measured **** spectrum is shown in drawing 1. It turned out that a spectrum becomes broadcloth more and can absorb light efficiently in the broad wavelength range as the sample number became large. In the wide wavelength range of 450-900 nm, ***** of a specific field is not only high, but has uniformly high ***** like the **** spectrum of the samples 1 and 3 in the samples 3, 5, 7, and 9 which are especially the RUTENIUMU phthalocyanine derivatives of this invention. Therefore, the application to the photoelectric conversion element etc. which can transform light energy into electricity efficiently is expectable.

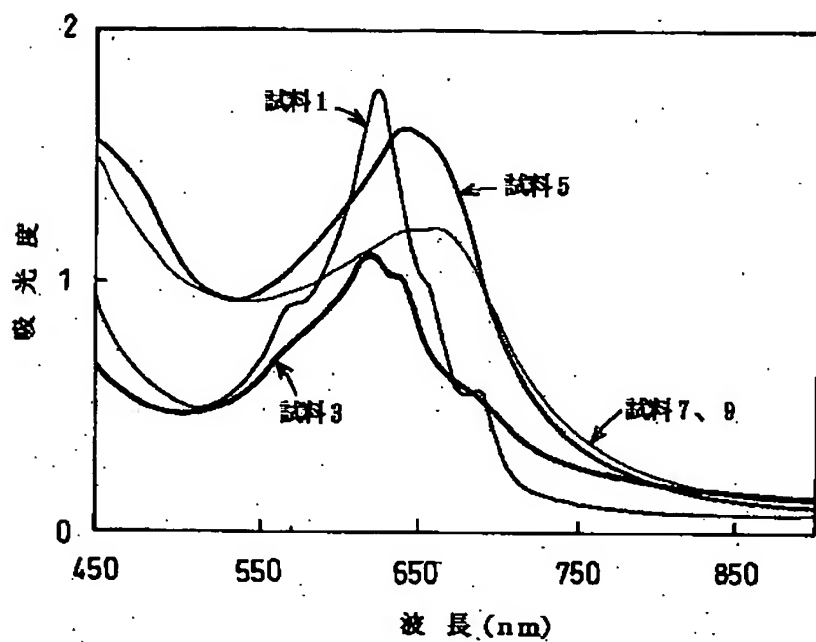
[0051]

[Effect of the Invention]As mentioned above, according to a RUTENIUMU phthalocyanine derivative of this invention, and a manufacturing method for the same, it has the effect that a new RUTENIUMU phthalocyanine derivative which raised the absorption efficiency over sunlight more, and a manufacturing method for the same can be provided.

[Brief Description of the Drawings]

[Drawing 1]It is a **** spectrum of each sample in an embodiment.

[Drawing 1]



[Translation done.]